

Scattering and Recombination of Two Triplet Excitons in polymer light-emitting diodes

Y.Meng,^{1,2,3} B.Di,^{1,3} X.J.Liu,^{1,3} Y.D.Wang,^{1,3} and Z. An^{1,3,*}

¹*College of Physics, Hebei Normal University, Shijiazhuang 050016, China*

²*Department of Physics, Xingtai University, Xingtai, 054001, China*

³*Hebei Advanced Thin Films Laboratory, Shijiazhuang 050016, China*

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The scattering and recombination processes between two triplet excitons in conjugated polymers are investigated by using a nonadiabatic evolution method, based on an extended Su-Schrieffer-Heeger model including interchain interactions. Due to the interchain coupling, the electron and/or hole in the two triplet excitons can exchange. The results show that the recombination induces the formation of singlet excitons, excited polarons and biexcitons. Moreover, we also find the yields of these products, which can contribute to the emission, increase with the interchain coupling strength, in good agreement with results from experiments.

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In recent years polymer semiconductors have made dramatic advances in light-emitting device performance, e.g., polymer light-emitting diodes (PLEDs) [1]. In these devices, following charge carrier recombination, singlet and triplet excitons are subsequently created. Compared to singlet excitons, which can decay radiatively and contribute to the emission, triplet excitons are nonluminescent. Although the precise ratio of singlets to triplets is currently debated, it has been established that triplet excitons constitute the dominant species in PLEDs [2–6]. Therefore, research into the dynamics of triplet excitons in conjugated polymers is urgently required.

Due to their long lifetime, a large number of the triplet excitons will accumulate in working PLEDs and have a significant probability of interacting and recombine with other particles. In our previous work [7], the recombining of a triplet exciton and a polaron was carefully investigated. Our results showed that the nonemissive triplet exciton is converted to emissive products, i.e., a singlet exciton and an excited polaron state. Therefore, the quantum efficiency of PLEDs can be enhanced by polaron-exciton recombination. In addition to this process, there is also another important case affecting the working characteristics of PLEDs, namely, triplet-triplet annihilation (TTA) [8–10]. These works have demonstrated that in PLEDs delayed fluorescence (DF) originates from the production of singlet excitons through the TTA process. Furthermore, Partee et al. [11] found that the DF intensity in films is higher than that in solutions. Accordingly, the triplet lifetimes are seen to decrease from solutions to films. In a recently performed experiment, Ribierre et al. [12] studied the effect of intermolecular spacing on the physics of exciton diffusion and light emission. They found the rate of TTA which is correlated to exciton diffusion, decreases with the intermolecular distance. These two works [11, 12] showed that both T-T annihilation by intermolecular recombination and the total emission are higher in the presence

of strong interchain interactions. Although some possible mechanisms for TTA processes have been proposed, no detailed theoretical investigations of how triplet exciton recombination affects quantum efficiency have been reported.

The goal of the present work is to investigate the recombination of two triplet excitons on two coupled chains and to address the branching ratio of the products. We use a nonadiabatic evolution method at the unrestricted Hartree-Fock level within an extended Su-Schrieffer-Heeger model including interchain interactions, with the extended Hubbard model for electron-electron interactions. Due to the interchain coupling, the electron and/or hole in the two triplet excitons can transfer between the two chains. As a result, the two triplet excitons can recombine to form singlet excitons, as well as excited polarons and biexciton states. These products are all luminescent due to radiative decay, which can enhance the efficiency of PLEDs. Furthermore, when compared with the results of experiments [8–11], which indicate that the DF derives from singlet excitons formed in TTA process, our results show that the primary source of DF is excited polarons.

The one chain model Hamiltonian we use is the Su-Schrieffer-Heeger (SSH) model [13] with a Brazoskii-Kirova-type symmetry-breaking term [14], including the effect of the intrachain electron-electron (e-e) interaction [15],

$$\begin{aligned}
 H = & - \sum_{j,n,s} t_n \left(c_{j,n,s}^\dagger c_{j,n+1,s} + c_{j,n+1,s}^\dagger c_{j,n,s} \right) \\
 & + \frac{K}{2} \sum_{j,n} (u_{j,n+1} - u_{j,n})^2 + \frac{M}{2} \sum_{j,n} \dot{u}_{j,n}^2 \\
 & + U \sum_{j,n} c_{j,n,\uparrow}^\dagger c_{j,n,\uparrow}^\dagger c_{j,n,\downarrow} c_{j,n,\downarrow} c_{j,n,\uparrow} \\
 & + V \sum_{j,n,s,s'} c_{j,n,s}^\dagger c_{j,n+1,s'}^\dagger c_{j,n+1,s'} c_{j,n,s}, \quad (1)
 \end{aligned}$$

Here, $j = 1, 2$ is the chain index. The quantity t_n is given by $t_n = t_0 - \alpha(u_{j,n+1} - u_{j,n}) + (-1)^n t_e$ with t_0 being the transfer integral of π -electrons in a regular lattice, α the electron-lattice coupling constant, and $u_{j,n}$ the lattice displacement of the atom at the n -th site along the j -th chain from its equidistant position. The quantity t_e is introduced to lift the ground-state degeneracy for nondegenerate polymers. The operator $c_{j,n,s}^\dagger (c_{j,n,s})$ creates (annihilates) a π -electron at the n -th site with spin s along the j -th chain; K is the elastic constant due to the σ bonds, and M is the mass of a CH group. U gives the strength of the on-site Coulomb interactions and V gives the strength of the nearest-neighbor interactions.

The two chains are coupled by the interchain interactions H' [16],

$$H' = - \sum_{n,s} t_\perp \left(c_{1,n,s}^\dagger c_{2,n,s} + c_{2,n,s}^\dagger c_{1,n,s} \right) + \sum_{n,s,s'} V_\perp c_{1,n,s}^\dagger c_{2,n,s'}^\dagger c_{2,n,s} c_{1,n,s}, \quad (2)$$

where t_\perp stands for the transfer integral between sites labelled by the same index n on the two chains and V_\perp is the e-e interaction term. In the following calculations V_\perp is fixed at 0.1eV.

The temporal evolution of the lattice is determined by the equation of motion for the atomic displacements,

$$M \ddot{u}_{j,n} = -K(2u_{j,n}(t) - u_{j,n+1}(t) - u_{j,n-1}(t)) + 2\alpha \sum_s [\rho_{jn,jn+1}^s(t) - \rho_{jn,jn-1}^s(t)], \quad (3)$$

where the density matrix ρ is defined as

$$\rho_{jn,j'n'}^s(t) = \sum_k \Phi_{j,n,k}^s(t) f_{k,s} \Phi_{j',n',k}^{s*}(t), \quad (4)$$

with $f_{k,s}$ being the time-independent distribution function as determined by the initial electron occupation. The electronic wave functions $\Phi_{j,n,k}^s(t)$ are the solutions of the time-dependent Schrödinger equation

$$i\hbar \dot{\Phi}_{j,n,k}^s(t) = \sum_{j',n'} h_{jn,j'n'}^s(t) \Phi_{j',n',k}^s(t). \quad (5)$$

The coupled differential equations (3) and (5) can be solved with a Runge-Kutta method of order 8 with step-size control [17]. The parameters used here are, $t_0 = 2.5\text{eV}$, $\alpha = 4.1\text{eV}/\text{\AA}$, $t_e = 0.05\text{eV}$, $K = 21\text{eV}/\text{\AA}^2$, and $M = 1349.14\text{eV} \cdot \text{fs}^2/\text{\AA}^2$.

In our numerical calculations, two 50-site parallel polymer chains opposite each other are considered: the CH-units are labeled as 1-50 on chain 1 and 51-100 on chain 2. We start with the stationary solution to the system after two triplet excitons are introduced, respectively, into chains 1 and 2. The initial bond configuration and electronic structure can be obtained by minimizing the total

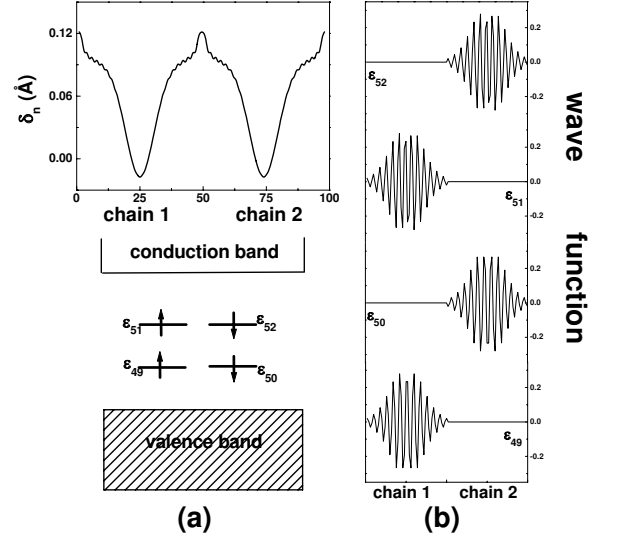


FIG. 1: (a) The staggered bond order parameters δ_n and schematic diagram of energy levels for the two triplet excitons; (b) The wave functions of the gap-state (from 49th energy level to 52th energy level).

static energy of the two-chain system in the absence of the interchain interactions.

Figure 1 (a) shows the initial staggered bond order parameters $\delta_n \equiv (-1)^n (u_{n-1} + u_{n+1} - 2u_n)/4$ and a schematic diagram of the energy levels for the two triplet excitons. In polymers, the exciton is a composite particle consisting of an electron and a hole bound together by a lattice deformation, due to the strong electron-lattice interactions. With the two deformations, four localized energy levels emerge in the energy gap. We consider the two excitons to have opposite spins (with $S_Z = +1$ and $S_Z = -1$). Obviously, there are two pairs of degenerate energy levels in the absence of interchain coupling. The corresponding wave functions are presented in Fig. 1 (b) [the 49th and 51st energy levels are localized on chain 1, and the 50th and 52nd energy levels are localized on the chain 2].

Then, turning on the interchain interactions, we simulate the charge transfer process and the dynamic relaxation of the recombination, with special attention given to the branching ratio of various species formed in the steady state. In order to avoid abrupt changes, the interchain coupling strength is smoothly increased over a period of 400fs, and then held at a constant value. As expected, due to the interchain coupling, the electron and/or hole in the two excitons will exchange between the two chains. That is to say, a portion of the spin-up electron and/or hole localized initially on chain 1 transfers to chain 2, and the spin-down electron and/or hole localized initially on chain 2 transfers partially to chain 1. Because the total charges on the two chains are equal initially, the effects of the interchain interactions only redistribute the electron and/or hole with different spin on

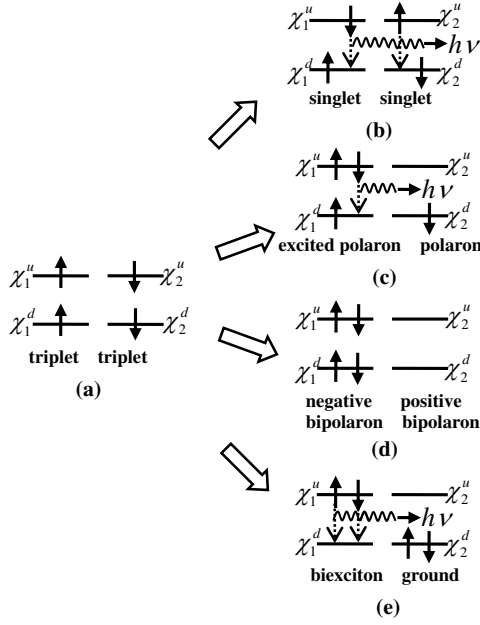


FIG. 2: The possible species of the recombination products of two triplet excitons.

the two chains and do not change the quantity of charge on each chain. Correspondingly, the amplitudes of the two lattice distortions for excitons are unchanged in the dynamical evolution processes. When the interchain coupling strength eventually increases to its final value, the charge transfer also reaches a maximum. At this point, the system approaches a dynamically stable state.

We now analyze the products of the recombination and determine the branching ratios for the formation of various species in the steady state. The approximate eigenstates χ_1 (localized on one chain) and χ_2 (localized on the other chain) can be separately obtained by ignoring the interchain coupling. It is found that such a structure is a mixture of sixteen possible states, i.e., an excited polaron localized on chain 1 and a polaron localized on chain 2, a polaron localized on chain 1 and an excited polaron localized on chain 2, etc. For simplicity, we divide these states into five species: (a) a triplet exciton on each chain, (b) a singlet exciton on each chain, (c) an excited polaron and a polaron, (d) a negative bipolaron and a positive bipolaron, and (e) a biexciton and a ground state, see Fig. 2 [only the gap-states, χ_1^u, χ_1^d for the particle localized on one chain, and χ_2^u, χ_2^d for the particle localized on another chain, are shown].

In order to ascertain the yields of these states, after each evolution step we can project the evolution wave functions $|\Phi(t)\rangle$ onto the space of the eigenstates of the system. The relative yield $I_K(t)$ for a given eigenstate $|\Psi_K\rangle$ is then obtained from

$$I_K(t) = |\langle \Psi_K | \Phi(t) \rangle|^2. \quad (6)$$

The evolved wave function of the whole system $|\Phi(t)\rangle$

can be constructed using the single electron evolution wave function $|\Phi_{j,n,k}^s(t)\rangle$ written as a Slater determinant. $|\Psi_K\rangle$ denotes the states of products shown in Fig. 2 (a)-(e). As an example, Fig. 3 shows how the yields of five species vary with time for the case $t_{\perp} = 0.1\text{eV}$. It may be seen that the yield of triplet excitons decreases, and simultaneously, the yields of the other four states increase as the interchain interactions are slowly increased. That is to say, the initial triplet excitons, due to interchain charge transfer, are transformed little by little into the other four states. After the interchain coupling strength reaches a constant value (at 400fs), the yields tend to be steady with only slight oscillations. In detail, the yields of the triplet exciton, the singlet exciton, the excited polaron, the bipolaron, and the biexciton are about 66.8%, 1.4%, 28.2%, 1.4%, and 1.4%, respectively.

It should be stressed that the excited polaron is luminescent as is the singlet exciton because they have comparable transition dipole moments (about $30\text{e}\text{\AA}$ for the singlet exciton and $54\text{e}\text{\AA}$ for the excited polaron). Furthermore, the biexciton state, in which two electrons and two holes are trapped together by a lattice distortion, can decay to the ground state by emitting two photons. Therefore, our results indicate that two nonemissive triplet excitons can be transformed into the emissive singlet exciton, the emissive excited polaron, and the emissive biexciton. Based on simple spin statistics arguments, the yield of the triplet exciton should be 75% and that of the singlet exciton should be 25% in PLEDs. When the recombination of two triplet excitons is taken into account, as stated above, for the case $t_{\perp} = 0.1\text{eV}$, two triplet excitons have a probability of about 31% of being converted into emissive species (28.2% to the excited polaron, 1.4% to the singlet exciton, and 1.4% to the biexciton, see fig. 3). Other processes also play a role. For example, in the recombination of the two excitons with parallel spin ($S_z = +1$ or $S_z = -1$), new products do not form. In contrast, for the recombination of the two excitons with $S_z = +1$ and $S_z = 0$, or $S_z = -1$ and $S_z = 0$, or both $S_z = 0$, the emissive excited polaron which is the primary product can be formed by charge exchange in the two chains. To summarize the above, in most processes where two triplet excitons recombine (with $S_z = +1, 0$, and -1), emissive products can be formed through interchain interactions. Therefore, the quantum efficiency of light-emitting diodes is enhanced, and the primary source of the increased efficiency is the excited polaron. Consequently, the experimental fact that the quantum efficiency exceeds 25% [18, 19] can be understood on the basis of recombination of two excitons.

With increasing interchain coupling strength, charge transfer between the two chains becomes easier, i.e., the transformation of various electron/hole states becomes easier. As a result, the products of the triplet-triplet recombination, i.e., the excited polaron, the singlet exciton,

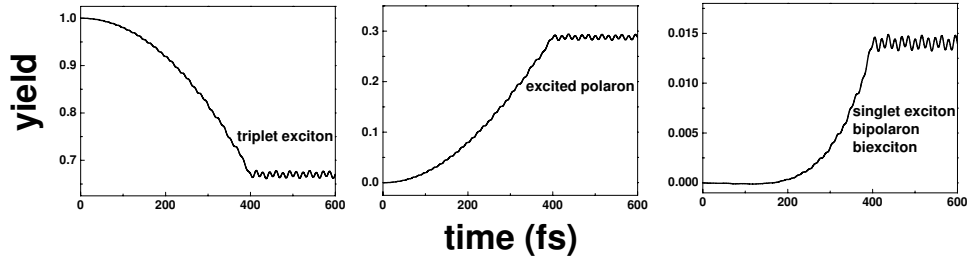


FIG. 3: The yields of five species vary with time in the case of $t_{\perp} = 0.1\text{eV}$.

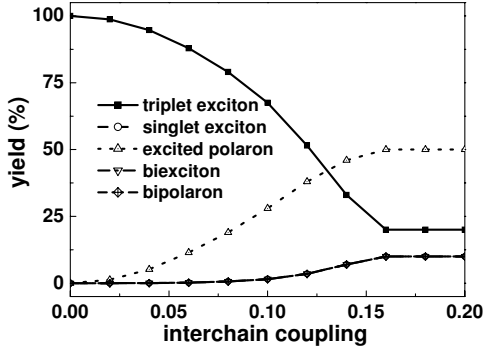


FIG. 4: The five species included in the final state as functions of the interchain coupling strength.

the bipolaron, and the biexciton increase with increasing interchain coupling strength, while the yield of the triplet exciton decreases, see Fig. 4. This implies that the interchain interaction greatly increases the formation of the emissive excited polarons, singlet excitons and biexcitons, and thus the quantum efficiency of devices. Our calculated results are in good agreement with the experimental observations [11, 12]. In ref 11 the delayed fluorescent of poly(p-phenylene vinylene) (PPV) and poly(p-phenylene ethynylene) (PPE) derivative solids and solutions was described. The results show that triplet-triplet bimolecular recombination induces the DF. Furthermore, the DF intensity in films is higher than that in solutions and the triplet lifetimes decrease from solutions to films. Reference 12 described the dynamics of triplet exciton quenching in phosphorescent dendrimers, in which the spacing of the emitting core was controllable. They found that as the distance between the cores increased, the rate of TTA decreased. These results showed that both T-T annihilation by intermolecular recombination and the total emission are higher in strongly interchain interactions. Therefore, our calculated results are indeed consistent with those found experimentally.

Finally, the effects of the e-e interactions on recombination are discussed. Depicted in Fig. 5 are the yields of the singlet exciton, which is equal to that of biexciton, and the excited polaron as functions of the on-site Hubbard energy U for different nearest neighbor Coulomb

interaction strengths V with $t_{\perp} = 0.1\text{eV}$. The value of U is allowed to range from 0 to 3.0 eV, and the relationships between U and V are $U=3.0\text{V}$ (solid line), $U=2.0\text{V}$ (dashed line), $U=1.5\text{V}$ (dotted line). It is found that the emissive singlet exciton, biexciton and the excited polaron are suppressed by U and V . The reason is that the binding energy of the electron and hole in a self-trapping excited state increases with the e-e interactions, making charge transfer between the two chains more difficult. Therefore, strong e-e interactions are unfavorable for the formation of the emissive species.

In conclusion, we have simulated the two triplet exciton recombination processes using a nonadiabatic evolution method. We have identified four types of products, of which the singlet exciton, the excited polaron, and the biexciton can decay radiatively. Our results indicate that the quantum efficiency of polymer light-emitting diodes is enhanced and can exceed 25% (the simple statistical limit) by the recombination of two triplet excitons. Furthermore, interchain interaction greatly increases the formation of emissive species, in good agreement with experimental observations. The effects of the e-e interactions on the recombination processes are also discussed.

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* Corresponding author. Email: zan@mail.hebtu.edu.cn

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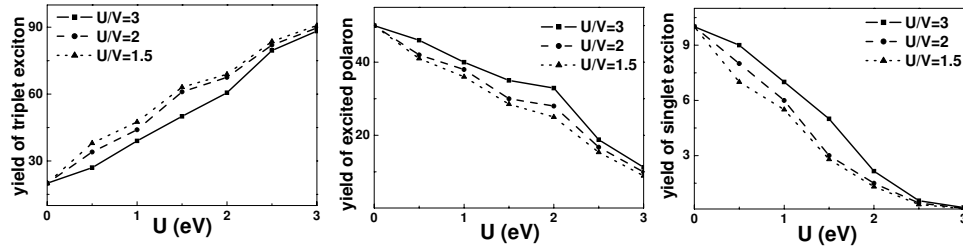


FIG. 5: The yields of the triplet exciton, singlet exciton and excited polaron with different e-e interactions.

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